Thermal Motion in Water + Electrolyte Solutions According to Quasi-Elastic Incoherent Neutron Scattering Data[†]

Tatjana V. Lokotosh,[‡] Nikolay P. Malomuzh,[‡] and Kirill N. Pankratov*[,§]

Department of Theoretical Physics, Odessa National University, 2 Dvoryanskaja str., Odessa 65026, Ukraine, and Odessa National Polytechnic University, 1 Shevchenko av., Odessa 65044, Ukraine

The main attention of this article is focused on the study of the physical mechanisms of thermal motion in water and water + electrolyte solutions that lead to the broadening of the incoherent neutron scattering peak. It is taken into account that the neutron peak has a diffusion nature and is described by a Lorentzian line shape only for wave vectors $\mathbf{k}$ having magnitudes $|\mathbf{k}| \equiv k \ll 1/a$, where a is the interparticle spacing. A modified version of the theory developed by Singwi and Sjolander (*Phys. Rev.* **1960**, *119*, 863) for the description of the Lorentzian half-width is proposed. It is shown that for $k > 1/a$, the neutron peak is described by a Gaussian line shape whose half-width is proportional to the average thermal velocity of the Lagrange particles. The relevant theoretical parameters can be determined by fitting experimental data for the half-width of the neutron peak. In such a way, the self-diffusion coefficients of water molecules, their collective parts, and the residence times as well as the radii of the Lagrange particles for the pure water and water + electrolyte solutions were determined. It is established that the specificity of the self-diffusion process in water + electrolyte solutions is mainly determined by the relation between a and the radius r_{I^+} of the cations I^+. The hydrated shell becomes more stable as the inequality $r_{I^+} < a/2$ becomes stronger. In the opposite case, its stability decreases. It is shown that the sizes of the Lagrange particles determined by different independent methods are consistent with each other. This fact is very important, since it testifies to the self-consistency of the obtained results.

Introduction

The investigation of the character of the thermal motion in water + electrolyte solutions has a long history. The circumstantial description of numerical experimental results and theoretical concepts is presented in the remarkable monograph by Barthel, Krienke, and Kunz.[1]

The goal of this paper is to complete our knowledge of this problem by the careful analysis of experimental data[2−12] obtained with the help of quasi-elastic incoherent neutron scattering. Our main attention is focused on the careful study of the temperature and concentration dependences of the following characteristics of the thermal motion in water + electrolyte solutions: the self-diffusion coefficient D_s of water molecules, its collective part D_c, and the residence time τ_0 for water molecules. These parameters have been determined by fitting the experimental data on the half-width of the neutron scattering peak to theoretical expressions.

In connection with this, we note that a theoretical model involving the parameters D_s and τ_0 was first developed by Singwi and Sjolander.[13] More definitely, in ref 13 it was supposed that the thermal motion in water and water + electrolyte solutions has crystal-like character, i.e., that a molecule oscillates near the temporary equilibrium position during the residence time, after which it shifts during a transition time $\tau_1 \ll \tau_0$ to another temporary equilibrium position. The theoretical model developed in ref 13 also includes an additional diffusion coefficient D_1 describing the random shift of a molecule during the transition time. The results of this work were used in refs 3−5 for the determination of D_s and τ_0.

The representations stated in ref 13 were generalized in ref 14, where it was noted that in addition to having relative motion with respect to its nearest neighbors, a molecule randomly drifts together with them in the field of thermal hydrodynamic fluctuations. It is necessary to emphasize that the notion of the collective transport is only applicable for liquids, in which fluctuation microflows arise. In particular, they are responsible for the stochastic drift of Brownian particles. According to ref 14, this process is characterized by the collective self-diffusion coefficient D_c. Thus, the full self-diffusion coefficient of a molecule should be considered as the sum of the relative (i.e., one-particle) and collective parts. The concept of collective transport in liquids was developed in detail in refs 15−18. The first attempt to determine the key theoretical parameters D_s, D_c, and τ_0 was undertaken in refs 8 and 9. It is necessary to note that D_s and τ_0 are also the key parameters for a model involving jumplike diffusion.[19]

Unfortunately, the results presented in refs 8, 9, and 11 and numerous other works are not quite reliable. This problem is caused by the circumstance that the experimental data for the half-width of the neutron peak have been fitted using theoretical formulas from refs 13 and 14 over the interval $0 < k^2 < 10$ Å^{-2}, where $k = |\mathbf{k}|$ is the magnitude of the wave vector $\mathbf{k}$; this interval is too large, since such fits are correct only for $0 < k^2 \ll (D_s\tau_0)^{-1} \approx 1$ Å^{-2}, as noted in refs 18, 20, and 21. This is obvious because the use of the diffusion concept on spatial scales smaller than the interparticle spacing [(1 to 3) Å] is meaningless from a physical point of view. Ignoring this circumstance leads to

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* Corresponding author. E-mail: betelgeyse@bk.ru.

[‡] Odessa National University.

[§] Odessa National Polytechnic University.

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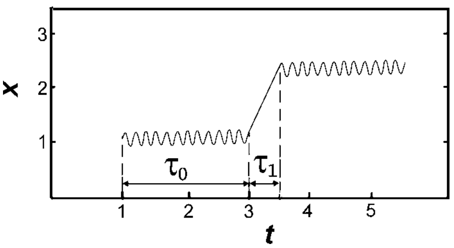

Figure 1. Crystal-like character of thermal motion in water (X is one of the components of the radius vector; it and the time t are given in arbitrary units).

considerable inaccuracies in the numerical values of the key theoretical parameters.[20,21]

In the present work, we present numerical values of D_s, D_c, and τ_0 obtained for water molecules in pure water and several water + electrolyte solutions, discuss the role of different ion parameters in the formation of the temperature and concentration dependences of the enumerated transport coefficients, and compare estimates of the size of the Lagrange particles obtained using several independent methods. The paper ends with a discussion of the results obtained, in which the main attention is focused on the physical nature of the self-diffusion in water + electrolyte solutions and the peculiarities of the hydration effects.

All of our calculations are based on the theoretical methods presented in two appendixes. In Appendix 1, we develop the consecutive diffusion model for the half-width of the quasi-elastic incoherent neutron scattering peak, which corresponds to crystal-like representations of the character of the thermal motion in water and water + electrolyte solutions. In Appendix 2, we derive a model for the half-width of the neutron peak outside region of applicability of the diffusion approximation [i.e., for $k^2 > (D_s\tau_0)^{-1} \approx 1\ \text{Å}^{-2}$].

Results

Qualitative Analysis of the Thermal Motion in Water. The character of the thermal motion in water is different in an essential way from that in argon and other simple liquids. This distinction is caused by the formation of H bonds. Because of them, as was established long ago,[22,23] the local structure of water near its melting point as well as in supercooled states is close to the regular structure in the hexagonal ice. There is also a similarity in the thermal motion: the oscillation motion of molecules is observed during the lifetime of local molecular configurations in liquid water.

Let τ_0 be the characteristic time for small oscillations of a molecule near its temporary equilibrium position. Often (including here), this time is called the residence time.[24] The characteristic time τ_1 during which a molecule is displaced from one vibration state to another will be called the transition time. The character of small oscillations in supercooled water is close to that in the hexagonal ice, where each molecule is connected with its nearest neighbors by four H bonds. However, the values of τ_0 in these two media are different: $\tau_0 = \infty$ for hexagonal ice but has a finite value for supercooled and normal water. One can say that the thermal motion in water has crystal-like character if $\tau_0 \gg \tau_1$. This situation is illustrated in Figure 1. An increase in temperature leads to a diminution of n_H, the average number of H bonds per molecule. However, till $n_H > 2$, the H-bond network remains to be ordered in the three-dimensional space.

In accordance with its physical meaning, the transition time τ_1 should be identified with the characteristic time of soft collisions between molecules: $\tau_s \approx a/v_T$, where v_T is the average value of the thermal velocity of a molecule. The value of τ_s weakly decreases as the temperature increases. In contrast to this, the residence time varies more considerably. It decreases as the temperature increases, and its value tends to the transition time τ_1.

The temperature T_H defined as the solution of the equation

$$\tau_0(T_H) = \tau_1(T_H) \tag{1}$$

specifies the upper temperature limit for the applicability of crystal-like representations. In other words, it can be interpreted as the temperature of the dynamic phase transition from the crystal-like picture of thermal motion in water to the argon-like one.

Let us estimate the numerical value of $\tau = \tau_0 + \tau_1$. Within an order of magnitude, the self-diffusion coefficient is given by $D_s \approx a^2/6\tau$. Since $D_s \approx 10^{-5}\ \text{cm}^2\cdot\text{s}^{-1}$ at room temperature for water and other usual liquids, it follows that

$$\tau \approx \frac{a^2}{6D_s} \approx 10^{-12}\ \text{s} \tag{2}$$

When the temperature decreases, the number of H bonds per molecule increases, and random drift of a molecule becomes more hindered. As a result, D_s decreases with temperature, leading to the growth of τ. Since τ_1 remains practically constant, we conclude that τ_0 should essentially increase as the temperature decreases.

For temperatures $T > T_H$, crystal-like representations of the thermal motion in water become inapplicable. In this temperature regime, the character of the thermal motion is similar to that in simple liquids, which do not form H bonds.

Thermal Motion in Pure Water. To determine the self-diffusion coefficient D_s, its one-particle part $D_s^{(1)}$, or its collective part $D_c = D_s - D_s^{(1)}$ along with the residence time τ_0, we fit the experimental data[5−7,11,12] for γ_D, the half-width of the diffusion peak, using eq A1.24. Since the number of experimental data points for $\gamma_D(k^2)$ with $k \ll 1\ \text{Å}^{-1}$ does not exceed 1 to 3, we used all of the points for which $k \leq 1\ \text{Å}^{-1}$. The numerical values of D_s, D_c, and τ_0 determined for different temperatures $T < T_H$, where $T_H \approx 315$ K,[20,25,26] are presented in Tables 1 to 3.

The values of D_s in Table 1 are in quite good agreement with those determined in the cited works, where they were calculated according to the formula $D_s = [\mathrm{d}\gamma_D(k^2)/\mathrm{d}k^2]_{k^2 \to 0}$. In contrast to this, the values of τ_0 presented in ref 12 differ considerably from our results in Table 1. For example, the following values of τ_0 were found: $2.4 \cdot 10^{-12}$ s at 274 K (ref 4) and $3 \cdot 10^{-12}$ s at 283 K (ref 5). Such a distinction is connected with the application of eq A1.21 far away from its applicability region. In the mentioned works, eq A1.21 was used in fitting experimental data over the range $0 < k^2 \leq 5\ \text{Å}^{-2}$. Attempts to determine the collective part of the self-diffusion coefficient D_c were first undertaken in refs 8, 9, and 14. Those values differ significantly from ours, as they also were obtained using a too-large interval of wave vectors. This circumstance was first noted in refs 18 and .

Detailed theoretical analyses of the collective self-diffusion problem are given in refs 15, 16, and 18. In particular, ref 18 gives the following expression for D_c:

$$D_c = \frac{k_B T}{10\pi\eta\sqrt{\nu\tau_M}} \tag{3}$$

in which k_B is the Boltzmann constant, η and ν are the dynamic and kinematic shear viscosities ($\nu = \eta/\rho$, where ρ is the density), and τ_M is the Maxwell relaxation time for shear tension.

Table 1. Values of the Self-Diffusion Coefficient D_s Determined from Fits of Experimental Data for the Half-Width of the Incoherent Neutron Scattering Peak Using Equation A1.24

	T/K									
	255	268	270	278	283	285	293	295	298	308
$10^5 \cdot D_s/\mathrm{cm^2 \cdot s^{-1}}$	0.97[a]	1.25[a]	1.77[b]	1.45[a]	2.25[b] 1.9[c]	1.83[a]	2.25[a] 2.35[d]	2.5[c]	2.3[e]	3.65[b] 4[c]

[a] Data from ref 7. [b] Data from ref 5. [c] Data from ref 12. [d] Data from ref 6. [e] Data from ref 11.

Table 2. Values of the Collective Part of the Self-Diffusion Coefficient D_c Determined from Fits of Experimental Data for the Half-Width of the Incoherent Neutron Scattering Peak Using Equation A1.24

	T/K									
	255	268	270	278	283	285	293	295	298	308
$10^5 \cdot D_c/\mathrm{cm^2 \cdot s^{-1}}$	0.08[a]	0.08[a]	0.1[b]	0.11[a]	0.12[b] 0.1[c]	0.16[a]	0.18[a] 0.21[d]	0.13[c]	0.2[e]	0.3[b] 0.2[c]

[a] Data from ref 7. [b] Data from ref 5. [c] Data from ref 12. [d] Data from ref 6. [e] Data from ref 11.

Table 3. Values of the Residence Time τ_0 Determined from Fits of Experimental Data for the Half-Width of the Incoherent Neutron Scattering Peak Using Equation A1.24

	T/K									
	255	268	270	278	283	285	293	295	298	308
$10^{12} \cdot \tau_0/\mathrm{s}$	7.2[a]	2.2[a]	1.3[b]	1.19[a]	0.85[b] 1.9[c]	0.69[a]	0.5[a] 0.45[d]	1.15[c]	0.7[e]	0.45[b] 1[c]

[a] Data from ref 7. [b] Data from ref 5. [c] Data from ref 12. [d] Data from ref 6. [e] Data from ref 11.

Table 4. Mean Square Displacement of a Molecule during the Elementary Diffusion Act and Ratio of the Self-Diffusion Coefficient to Its Collective Part Calculated According to Reference 7

T/K	268	278	285
$6D_s\tau \cdot 10^{16}/\mathrm{cm^2}$	1.65	1.04	0.76
D_s/D_c	15.62	13.18	11.44

Table 5. Values of the Parameters for Dilute Water + Electrolyte Solutions at $T = 298$ K Obtained on the Basis of Experimental Data from Reference 11

electrolyte	r_{I^+} Å	z_w	$10^5 \cdot D_s$ $\mathrm{cm^2 \cdot s^{-1}}$	$10^5 \cdot D_c$ $\mathrm{cm^2 \cdot s^{-1}}$	$10^{12} \cdot \tau_0^{(w)}$ s
LiCl	0.78	55.6	2.15	0.95	0.8
		27.8	1.95	0.85	1.2
NaCl	0.98	27.8	2	0.45	0.7
		13.9	1.75	0.43	0.9
CsCl	1.65	27.8	2.35	0.25	0.7

According to refs 18 and 21, the temperature dependence of τ_M can be approximated by the formula

$$\tau_M(T) = \tau_M(T_0)\left(\frac{\nu(T)}{\nu(T_0)}\right)^{3/4} \tag{4}$$

However, such a simple temperature dependence probably takes place only for one-component liquids. If a system has two or more components, its shear viscosity and viscoelastic modulus change. The framework of the Maxwell construction gives $\tau_M = \eta/G$, which shows that the temperature dependence of τ_M is determined by both the shear viscosity and the high-frequency shear modulus G. In particular, the addition of an electrolyte to water is accompanied by an increase in its density,[27,28] which would be expected to lead to an increase in G.

It should be noted that H bonds limit the value of the displacement of a molecule during the elementary diffusion act. To an order of magnitude, the corresponding mean square displacement $\langle \Delta r_1^2 \rangle^{1/2} \approx (6D_s\tau)^{1/2}$ of a molecule should not exceed the H-bonding length (i.e., about 1 Å). The estimates given in Table 4 testify that this condition is satisfied by the experimental data in refs 5 and 7.

To an order of magnitude, the ratio D_s/D_c is proportional to the ratio $\tilde{r}_L = r_L/r_w$ of the Lagrange particle radius to the radius of a molecule. This quantity can be found independently from the analysis of the half-widths for the neutron peak over the range $k > 1$ Å^{-1} (as discussed in the next section).

Peculiarities in the Thermal Motion of Water Molecules in Water + Electrolyte Solutions. This section is devoted to a consideration of peculiarities in the diffusion of water molecules in water + electrolyte solutions, for which numerous experimental data have been obtained using quasi-elastic incoherent neutron scattering.

We expect the thermal motion of water molecules in water + electrolyte solutions to also have crystal-like character, since, like H bonds, the electric field of the ions holds water molecules in the vicinity of the ions. It is necessary to take into account the fact that the temporary equilibrium position of a water molecule can be situated in either bulk water (w) or the hydration shell of an ion (h). In correspondence with this, we differentiate between the residence times $\tau_0^{(w)}$ and $\tau_0^{(h)}$, which depend on the ion concentrations.

It seems evident that for dilute water + electrolyte solutions, the diffusion peak is mainly formed by molecules from the bulk water. Therefore the half-width of the diffusion peak is given by

$$\gamma_D(k^2) \approx D_s k^2 - \tau_0^{(w)} D_s^{(1)2} k^4 + \tau_0^{(w)2} D_s^{(1)3} k^6 + ... \tag{5}$$

where all designations are analogous to those in eq A1.24. In the opposite case, when practically all of water molecules are in the hydrate shells, eq A1.24 becomes

$$\gamma_D(k^2) \approx D_s k^2 - \tau_0^{(h)} D_s^{(1)2} k^4 + \tau_0^{(h)2} D_s^{(1)3} k^6 + ... \tag{6}$$

It seems to be evident that the character of the thermal motion of water molecules in dilute water + electrolyte solutions should change insignificantly relative to that in pure water. Therefore, the values of the main parameters D_s, $D_s^{(1)}$ [or $D_c = D_s - D_s^{(1)}$], and $\tau_0^{(w)}$ are expected to be close to those for pure water. This supposition is partially confirmed by values of D_s and $\tau_0^{(w)}$ collected in Table 5 (in this table and elsewhere, the concentration of electrolyte is expressed in terms of z_w, the number of water molecules per ion). Comparison with the corresponding parameters for pure water at the close temperature $T = 293$ K ($D_s = 2.2 \cdot 10^{-5}$ cm$^2 \cdot$s^{-1}, $D_c = 0.17 \cdot 10^{-5}$ cm$^2 \cdot$s^{-1}, and $\tau_0 = 0.8 \cdot 10^{-12}$ s) shows that only the values of D_c in water + electrolyte solutions differ significantly from those in pure water.

The concentration dependences of the enumerated parameters at another temperature ($T = 274$ K) are presented in Table 6.

Table 6. Concentration Dependences of D_s, D_c, and τ_0 for Water Molecules in Water + Electrolyte Solutions at $T = 274$ K Obtained on the Basis of Experimental Data from Reference 4

electrolyte	z_w	$10^5 \cdot D_s$ / $\mathrm{cm^2 \cdot s^{-1}}$	$10^5 \cdot D_c$ / $\mathrm{cm^2 \cdot s^{-1}}$	$10^{12} \cdot \tau_0^{(e)}$ / s
CsCl	55.6	1.2	0.2	1.8
	11.1	1.35	0.25	1.6
	6.05	1.4	0.3	1.5
	2.9	1.5	0.3	1.2
NaCl	5.9	1.2	0.17	1.45
	6.05	1	0.15	1.8
	4.54	0.85	0.12	2.4
LiCl	55.6	1,1	0.07	1.2
	9.27	1	0.16	1.9
	6.05	0.9	0.18	2.3
	2.78	0.5	0.21	9
	1.85	0.27	0.12	24

Table 7. Concentration Dependences of the Self-Diffusion Coefficients for Water Molecules in Water + Electrolyte Solutions at 296 K Given in Reference 35

z_w	$10^5 \cdot D_s(\mathrm{LiCl})$ / $\mathrm{cm^2 \cdot s^{-1}}$	z_w	$10^5 \cdot D_s(\mathrm{NaCl})$ / $\mathrm{cm^2 \cdot s^{-1}}$	z_w	$10^5 \cdot D_s(\mathrm{KCl})$ / $\mathrm{cm^2 \cdot s^{-1}}$
49.6	2.27	126.3	2.36	126.3	2.48
24.8	2.18	64.6	2.4	64.7	2.49
9.93	1.75	32.2	2.29	32.3	2.4
4.96	1.13	16	2.14	16.1	2.44
2.48	0.31	8	1.8	8.1	2.38

Here $\tau_0^{(e)}$, the residence time for the electrolyte solution (e), coincides with $\tau_0^{(w)}$ for dilute solutions and $\tau_0^{(h)}$ for concentrated ones. As we can see, the values of D_s and τ_0 for very dilute solutions are close to those for pure water ($D_s = 1.37 \cdot 10^{-5}$ $\mathrm{cm^2 \cdot s^{-1}}$ and $\tau_0 = 1.18 \cdot 10^{-12}$ s). The distinction between the values of D_c for pure water ($D_c = 0.1 \cdot 10^{-5} \mathrm{cm^2 \cdot s^{-1}}$) and dilute water + electrolyte solutions is significantly smaller here than in Table 5. From a physical point of view, the values of D_c from Table 6 seem to us more suitable.

It is appropriate to complete our results by examining the concentration dependences of the self-diffusion coefficients for water molecules in water + electrolyte solutions that were presented in ref 29 (see Table 7). The data show a strong concentration dependence of D_s for the water + LiCl solution, a significantly weaker dependence for water + NaCl, and a practically constant value of D_s for water + KCl.

It seems to be natural to connect such behavior of D_s and τ_0 with the radius of cations. More definitely, we suppose that the key role is played by the relation between the cation radius r_{I^+} and r_w, defined as half of the interparticle spacing between the nearest neighbors in pure water, which is approximately equal to 1.4 Å. As Tables 5 and 8 show, the radius of the K^+ cation is very close to r_w, so for it the concentration dependence for D_s is practically absent. In addition, we can see the following: (1) Addition of electrolyte (i.e., decreasing z_w) leads to a decrease in the self-diffusion coefficient of water molecules for all of the water + electrolyte solutions in which the cation radius is smaller than r_w. This effect is more pronounced as the inequality $r_{I^+} < r_w$ becomes stronger. (2) The increase in the residence times of water molecules with increasing electrolyte concentration in water + electrolyte solutions for which $r_{I^+} < r_w$ testifies to the stabilization of molecular configurations upon the addition of electrolyte. (3) The influence of cations for which $r_{I^+} > r_w$ is the opposite. The addition of such electrolytes should lead to the destruction of molecular configurations. From this point of view, the concentration dependences of D_s and $\tau_0^{(e)}$ for the water + CsCl solution becomes quite clear.

Table 8. Values of the Self-Diffusion Coefficients, Their Collective Parts, and the Residence Times for Concentrated Water + Electrolyte Solutions

electrolyte	T / K	r_{I^+} / Å	z_w	$10^5 \cdot D_s$ / $\mathrm{cm^2 \cdot s^{-1}}$	$10^5 \cdot D_c$ / $\mathrm{cm^2 \cdot s^{-1}}$	$10^{12} \cdot \tau_0^{(h)}$ / s	ref
LiCl	348	0.78	6.05	4.6	1.05	0.6	3
	323			2.5	0.5	0.8	
	298			1.9	0.37	2	
	274			0.8	0.15	2.3	
	298		5.56	1.05	0.90		11
NaCl	348	0.98	6.05	4.6	1.5	1	3
	323			2.7	0.75	1.2	
	298			1.9	0.35	1.6	
	274			0.9	0.15	1.8	
KCl	348	1.33	6.05	4.3	1.1	0.6	3
	323			3.4	0.8	0.7	
	298			2.4	0.3	0.8	
	274			1	0.1	0.9	
CsCl	348	1.65	6.05	4.05	0.8	0.5	3
	323			3.4	0.65	0.6	
	298			2.7	0.3	0.9	
	274			1.2	0.1	1.1	
	298		5.56	3.10	0.3	0.2	11
	298		3.48	2.80	0.45	0.8	

Table 9. Temperature Dependences of D_s, D_c, and τ_0 for Pure Water

T/K	$10^5 \cdot D_s$ / $\mathrm{cm^2 \cdot s^{-1}}$	$10^5 \cdot D_c$ / $\mathrm{cm^2 \cdot s^{-1}}$	$10^{12} \cdot \tau_0$ / s
348	7.3	1.2	–
323	5.4	0.7	0.2
298	2.2	0.18	0.5
274	1.3	0.07	2

To clear up the role of the shear viscosity in the self-diffusion process, let us compare the ratios of the self-diffusion coefficients of water molecules in electrolyte solutions and pure water with the corresponding ratios of the shear viscosity coefficients. At $T = 296$ K and $z_w = 27$, we find the following from refs 28 and 29:

$$\frac{D_s(\text{water + LiCl})}{D_s(\text{water})} = 0.94, \quad \frac{D_s(\text{water + NaCl})}{D_s(\text{water})} = 0.95, \quad \frac{D_s(\text{water + KCl})}{D_s(\text{water})} = 1.02$$

and

$$\frac{\eta(\text{water})}{\eta(\text{water + LiCl})} = 0.85, \quad \frac{\eta(\text{water})}{\eta(\text{water + NaCl})} = 0.92, \quad \frac{\eta(\text{water})}{\eta(\text{water + KCl})} = 0.99.$$

Thus, the behavior of the self-diffusion coefficients does not follow that of the shear viscosities. We see again that the cation sizes influence the values of these kinetic coefficients in an essential way. This problem needs the careful study.

The variation of the parameters of the thermal motion with temperature in concentrated water + electrolyte solutions ($z_w = 6.05$) is presented in Table 8. The corresponding values of the same parameters for pure water, taken from Tables 1 to 3, are collected in Table 9. From Tables 8 and 9, it follows that the temperature dependences of all of the considered parameters are more trivial: (1) D_s and D_c increase with temperature, and (2) $\tau_0^{(h)}$ decreases when as the temperature increases. Also, the temperature dependence of $\tau_0^{(h)}$ is significantly weaker than for pure water. This means that H bonds play a considerably lesser role in concentrated solutions, where the character of the thermal motion of the water molecules is determined by the influence of the electric field of the ions. The close values of D_s for different water + electrolyte solutions is the most characteristic

Table 10. Self-Diffusion Coefficient of Li^+ as a Function of Temperature and Concentration (Data from Reference 30)

	z_w					
	8.18		5.72		4.02	
T/K	278	303	281	298	280	293
$10^5 \cdot D_{Li^+}/cm^2 \cdot s^{-1}$	0.4	0.7	0.3	0.5	0.17	0.25

Table 11. Reduced Radii $\tilde{r}_L = r_L/r_w$ of the Lagrange Particles for Pure Water as a Function of Temperature (Experimental Data for γ_n and the Crossover Wave Vector Magnitude k_{cr} Were Taken from Reference 5)

T/K	308	329	348	368
$10^{-8} \cdot k_{cr}/cm^{-1}$	1.3	1.5	1.5	1.8
$10^{-3} \cdot (d\gamma_n/dk)/cm \cdot s^{-1}$	11	9.6	12.8	22.9
$\tilde{r}_L$	7.2	8	6.7	4.6

feature of the self-diffusion. It testifies that the peculiarities of the hydrated shells at $z_w = 6$ only weakly depend on the cation radii. In addition, the numerical values of D_s in concentrated water + electrolyte solutions are approximately two-thirds those in pure water.

Here it is appropriate to compare the collective parts of the self-diffusion coefficients for water molecules with those for cations. The corresponding experimental data for the self-diffusion coefficient of Li^+ are presented in Table 10. Comparing Tables 6 and 10, we see that the values of D_c for water molecules in water + LiCl solutions coincide with those of the self-diffusion coefficient D_{Li^+} for Li^+ within experimental error, which obviously indicates that the collective drift of water molecules in concentrated water + electrolyte solutions is immediately connected with movement of ions. At the same time, it is not correct to speak about the long-lived hydration shell. Actually, the self-diffusion coefficient of water molecules is significantly greater than D_{Li^+} (by a factor of 3 to 4; see Table 8). In fact, one speaks about the hydration shell only over a period close to the residence time τ_0 for water molecules.

Let us conclude this discussion of the peculiarities of the diffusion motion of water molecules in water and water + electrolyte solutions by considering the neutron peak structure for $k > 1$ Å^{-1}. It was noted in ref 5 that for these wave vectors, the half-width of the neutron peak changes linearly with respect to the magnitude of the wave vector k. In accordance with eq A2.4, when $k > 1$ Å^{-1}, the mass of a Lagrange particle m_L is connected to the half-width of the neutron peak γ_n through the relation

$$m_L = \frac{12 k_B T}{(d\gamma_n/dk)^2} \tag{7}$$

The radius of the Lagrange particle is trivially determined from m_L and the density as $r_L = (3m_L/4\pi\rho)^{1/3}$. The corresponding estimates of r_L for pure water are presented in Table 11.

In accordance with the Lagrange theory of thermal hydrodynamic fluctuations (see ref 18), $r_L = 2(\nu\tau_M)^{1/2}$. To an order of magnitude, the value of the Maxwell relaxation time is expected to be close to the residence time. In accordance with this and the data in Table 3, we set $\tau_M \approx 4.5 \cdot 10^{-13}$ s at $T = 308$ K. For higher temperatures, the values of the Maxwell relaxation time can be calculated according to eq 4. Since $\nu \approx 0.74 \cdot 10^{-2}$ cm$^2 \cdot$s^{-1} at $T = 308$ K, we find that $\tilde{r}_L \approx 8.3$. This number is also consistent with the extrapolated values of D_s/D_c from Table 4. Thus, full agreement between the predictions of the Lagrange theory of thermal hydrodynamic fluctuations and the results given by neutron scattering theory is observed. For other temperatures, the agreement is also quite satisfactory.

Table 12. Reduced Radii $\tilde{r}_L = r_L/r_w$ of Lagrange Particles in Water + LiCl Solutions as a Function of Temperature [Experimental Data for γ_n and the Crossover Wave Vector k_{cr} Were Taken from Reference 3 ($z_w = 6.05$)]

T/K	274	298	323	348
$10^{-8} \cdot k_{cr}/cm^{-1}$	1.18	1.18	1.18	1.18
$10^{-3} \cdot (d\gamma_n/dk)/cm \cdot s^{-1}$	1.13	2.04	2.87	3.17
$\tilde{r}_L$	30.14	20.93	17.2	16.57

The half-width of the neutron peak in water + electrolyte solutions is also linear with respect to k for $k > 1$ Å^{-1}. In this case, the radius of the Lagrange particle, calculated as $r_L = 2(\nu\tau_M)^{1/2}$ with the assumption that $\tau_M \approx \tau_0^{(h)}$ for all temperatures, is also in good agreement with the data collected in Table 12. In particular, for $T = 274$ K, setting $\tau_M = 2.3 \cdot 10^{-12}$ s gives a value of $\tilde{r}_L = 28.6$ for the reduced radius of the Lagrange particle, which practically coincides with corresponding value from Table 12.

Here it is necessary to note that the reduced radii of Lagrange particles in water + electrolyte solutions differ significantly from the values of $R_D = D_s(w + e)/D_c(w + e)$. The data in Table 8 for concentrated water + electrolyte solutions give $R_D \approx 4$ to 10, which is approximately half that for pure water. This means that the collective transport in water + electrolyte solutions has a more complicated character. Indeed, in such solutions, the thermal motion of ions leads to an additional mechanism of collective transport for water molecules, due to which the collective part of the self-diffusion coefficient of the water molecules is close to the self-diffusion coefficient of the ions, as noted above. This question needs separate careful study.

Discussion

In this paper, the main attention has been focused on those peculiarities of the thermal motion in water + electrolyte solutions that can be established with the help of quasi-elastic incoherent neutron scattering. More definitely, by studying the behavior of the half-width of the neutron peak, we have determined the temperature and concentration dependences of the self-diffusion coefficient of water molecules D_s, its collective part D_c, and the residence time τ_0.

For this purpose, we have revised the theory of incoherent neutron scattering for crystal-like character of the thermal motion in liquids that was developed in ref 13, taking into account the fact that the region of applicability of the diffusion approximation is restricted to wave vectors $\mathbf{k}$ for which $k \ll 1/a$, where a is the interparticle spacing. Analyzing the temperature and concentration dependences of D_s, D_c, and τ_0 for water molecules in water + electrolyte solutions has shown that their behavior is mainly determined by the size of the cations and changes in the H-bonding network. In particular, the latter is responsible for the considerable changes in D_s and D_c over comparatively narrow temperature intervals. One can show that our estimates for the average number of H bonds per molecule are in good agreement with those in ref 31.

We have shown that the diffusion Lorentzian line shape observed for $k \ll 1/a$ changes to a Gaussian line shape for $k > 1/a$. Moreover, the half-width of the Gaussian peak proves to be proportional to the thermal velocity V_L of the Lagrange particles: $\gamma_n \approx V_L k$. Therefore, using the wave-vector-dependence of the half-width enables us to determine the average size of the Lagrange particles. The notion of a Lagrange particle is very important in the Lagrange theory of thermal hydrodynamic fluctuations, which was created for the description of collective transport in liquids. Therefore, the possibility of scanning Lagrange particles in neutron experiments can be considered as experimental evidence of their existence.

Such a situation is also characteristic of concentrated water + electrolyte solutions. However, the collective drift of molecules in these solutions is not connected with only the thermal motion of Lagrange particles. The thermal motion of ions is accompanied by the additional transport of water molecules. This fact is obviously certified by the closeness of the collective part of the self-diffusion coefficient for water molecules and the self-diffusion coefficient for cations. This question needs more detailed study.

On the basis of our analysis of the concentration dependences of D_s, D_c, and τ_0 for water molecules in different water + electrolyte solutions, we have concluded that the size of the cation renders the key influence on the mobility of water molecules. More exactly, if the cation radius is smaller than r_w, defined as half the interparticle spacing in pure water (which happens to be equal to the radius of K^+), the stability of the hydrated complex increases as the inequality $r_{I^+} < r_w$ becomes stronger. In the opposite case, the hydrated complexes become unstable, and the molecular exchange between different hydrated shells is essentially forced. It is necessary to emphasize that the notion of the hydration shell has meaning only for time scales on the order of τ_0.

A similar dependence on the cation radius is inherent in the hydration energy of ions, as determined by chemical methods.[38] The microscopic nature of this effect is discussed in refs 39−42. The results of refs 41 and 42 seem to us to be especially successful.

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Appendix 1.

Differential Cross Section for Quasi-Elastic Incoherent Neutron Scattering.

Here we construct the differential equation for the intermediate scattering function,[37,38]

$$F_s(\mathbf{k}, t) = \langle \exp[i\mathbf{k}\cdot\Delta\mathbf{r}(t)] \rangle \tag{A1.1}$$

which should correspond to the picture of the thermal motion described in the main text. In eq A1.1, **k** is the wave vector of the neutron and $\Delta\mathbf{r}(t)$ is the time-dependent displacement vector of a molecule.

In general, the displacement vector $\Delta\mathbf{r}(t)$ can be represented as the sum of two terms

$$\Delta\mathbf{r}(t) = \Delta\mathbf{r}^{(v)}(t) + \Delta\mathbf{r}^{(d)}(t)$$

where the first term represents displacements caused by vibrational modes and the second term corresponds to the irreversible thermal drift from one temporary equilibrium position to another. Since these contributions are statistically independent, the intermediate function given by eq A1.1 can be transformed into the product

$$F_s(\mathbf{k}, t) = \langle \exp[i\mathbf{k}\cdot\Delta\mathbf{r}^{(v)}(t)] \rangle \langle \exp[i\mathbf{k}\cdot\Delta\mathbf{r}^{(d)}(t)] \rangle \tag{A1.2}$$

In the long-time limit,

$$\tau_1 \ll \tau_0 \ll t \tag{A1.3}$$

the average $\langle \exp[i\mathbf{k}\cdot\Delta\mathbf{r}^{(v)}(t)] \rangle$ does not depend on time and takes the form

$$\langle \exp[i\mathbf{k}\cdot\Delta\mathbf{r}^{(v)}(t)] \rangle \rightarrow \exp\left(-\frac{k^2}{6}\langle \Delta r^{(v)}(t)^2 \rangle\right) \equiv \exp(-2W) \tag{A1.4}$$

where $k = |\mathbf{k}|$ and $\Delta r(t) = |\Delta\mathbf{r}(t)|$; in other words, this average generates the standard Debye−Waller factor.[37]

In the same limit, the irreversible shifts of a molecule are characterized by the Gaussian distribution

$$W[\Delta\mathbf{r}^{(d)}(t)] = \left(\frac{\alpha}{\pi}\right)^{3/2} \exp[-\alpha \Delta r^{(d)}(t)^2] \tag{A1.5}$$

where D_s is the self-diffusion coefficient of a molecule and $\alpha = (4D_s t)^{-1}$. In this case, it follows from eq A1.5 that

$$\langle \exp[i\mathbf{k}\cdot\Delta\mathbf{r}^{(d)}(t)] \rangle = \exp(-D_s k^2 t) \tag{A1.6}$$

The twice-differential cross section for quasielastic incoherent (inc) neutron scattering corresponding to eqs A1.2, A1.4, and A1.6 is proportional to a Lorentzian function:

$$\left(\frac{d^2\sigma}{d\Omega\, d\varepsilon}\right)_{inc} = \frac{{b_{inc}}^2 k}{\pi\hbar k_0} \exp(-2W) \frac{\gamma_D}{\omega^2 + {\gamma_D}^2} \tag{A1.7}$$

where $\hbar$ is Planck's constant, k_0 and k are the magnitudes of the initial and final wave vectors of the neutron, respectively, b_{inc} is the bound incoherent scattering length, and $\gamma_D(k^2)$ is the half-width of the Lorentzian, given by

$$\gamma_D(k^2) \approx D_s k^2 \tag{A1.8}$$

It should be noted that eq A1.7 correctly describes the influence of the oscillation motion of molecules on the integral intensity of the neutron scattering:

$$\left(\frac{d\sigma}{d\Omega}\right)_{inc} = \frac{{b_{inc}}^2 k}{\hbar k_0} \exp(-2W)$$

It is now relevant to discuss the applicability region of the diffusion approximation. It follows from eq A1.3 that the applicability region of the Lorentzian in eq A1.7 is restricted by the inequality

$$\omega \ll \frac{1}{\tau_0} \tag{A1.9}$$

which together with eq A1.8 leads to the following important restriction on the magnitude of the wave vector:

$$k \ll \frac{1}{\sqrt{D_s \tau_0}} \tag{A1.10}$$

From the definition of D_s, the quantity $(D_s\tau_0)^{1/2}$ is proportional to the shift of a molecule during an elementary diffusion act. Since such a displacement does not exceed the interparticle spacing a, the inequality A1.10 can be rewritten in the form:

$$k \ll \frac{1}{a} \approx 1\ \text{Å}^{-1} \tag{A1.11}$$

Thus, the applicability region of the simplest diffusion approximation coincides with that for the continuous medium.

To extend the applicability region of the diffusion approach, i.e., to describe the wings of the diffusion peak in the frequency range

$$\omega < \frac{1}{\tau_0} \quad \text{or} \quad k < \frac{1}{\sqrt{D_s\tau_0}} \qquad \text{(A1.12)}$$

we should include in our consideration effects that reflect the crystal-like character of the thermal motion in water and water + electrolyte solutions. More definitely, it is necessary to construct an expansion of the half-width of the diffusive peak with respect to powers of the small parameter $\mu = \tau/[\tau_D(k^2)] \equiv \tau D_s k^2$:

$$\gamma_D(k^2) = D_s k^2[1 + a_1\mu(k^2) + a_2\mu^2(k^2) + ...] \qquad \text{(A1.13)}$$

The method allowing us to realize our intention has been borrowed from ref 19.

An elementary diffusion act, as described in the main text, can be introduced into our considerations if we start from the approximate equation for the intermediate scattering function:

$$\frac{\partial F_s(\mathbf{k}, t)}{\partial t} = \frac{1}{\tau}[F_s(\mathbf{k}, t + \tau) - F_s(\mathbf{k}, t)] \qquad \text{(A1.14)}$$

Now our efforts will be directed toward the determination of an explicit expression for the difference $F_s(\mathbf{k}, t + \tau) - F_s(\mathbf{k}, t)$ as a function of t, τ, and k^2.

The displacement $\mathbf{\Delta r}(t)$ of a molecule in time t can be represented as the sum:

$$\mathbf{\Delta r}(t) = \mathbf{\Delta r}(t_{1,2}) + \mathbf{\Delta r}(t_{2,3}) + ... + \mathbf{\Delta r}(t_{N-1,N})$$

where $\mathbf{\Delta r}(t_{i-1,i}) = \mathbf{r}(t_i) - \mathbf{r}(t_{i-1})$ is the displacement during the ith elementary diffusion act. In accordance with what was said above, every contribution $\mathbf{\Delta r}(t_{i-1,i})$ is split into two terms:

$$\mathbf{\Delta r}(t_{i-1,i}) = \mathbf{\Delta r}^{(v)}(t_{i-1,i}) + \mathbf{\Delta r}^{(d)}(t_{i-1,i})$$

On average, $\langle t_{i-1,i}\rangle = \langle t_i - t_{i-1}\rangle = \tau$. Let us suppose that (1) the typical periods of oscillation satisfy the inequality $\tau_v \ll \tau_0$ and (2) the displacements $\mathbf{\Delta r}(t_{i-1,i})$ and $\mathbf{\Delta r}(t_{j-1,j})$ for $j \neq i$ are statistically independent. On the basis of the first assumption, $\langle\mathbf{\Delta r}^{(v)}(t_{i-1,i})\rangle$ should not depend on the duration of the ith interval:

$$\left\langle \exp[\mathrm{i}\mathbf{k}\cdot\mathbf{\Delta r}^{(v)}(t_{i-1,i})]\right\rangle \rightarrow \exp(-2W)$$

On the basis of the second assumption, the intermediate function at time $t_N = N\tau$ can be written as

$$F_s(\mathbf{k}, t_N) \rightarrow \exp(-2W)F_d(\mathbf{k}, t_N) \qquad \text{(A1.15)}$$

in which

$$F_d(\mathbf{k}, t_N) = [f_1(k^2)]^N$$

where

$$f_1(k^2) = \left\langle \exp[\mathrm{i}\mathbf{k}\cdot\mathbf{\Delta r}^{(d)}(t_{1,2})]\right\rangle$$

From this it follows that $F_d(\mathbf{k}, t_j)$ for $1 \leq j \leq N$ has the structure:

$$F_d(\mathbf{k}, t_j) = F_d(\mathbf{k}, t_{j-1})f_1(k^2) \qquad \text{(A1.16)}$$

Substituting eq A1.16 into A1.14, we obtain the following approximate differential equation for the intermediate scattering function $F_s(\mathbf{k}, t)$:

$$\left.\frac{\partial F_d(\mathbf{k}, t)}{\partial t}\right|_{t=t_j} = -\frac{1}{\tau}F_d(\mathbf{k}, t_j)[1 - f_1(k^2)]$$

This leads to the solution

$$F_d(\mathbf{k}, t) = \exp\left(-\frac{[1 - f_1(k^2)]}{\tau}t\right)$$

which gives the following expression for the half-width of the diffusion peak:

$$\gamma_D(k^2) = \frac{1 - f_1(k^2)}{\tau} \qquad \text{(A1.17)}$$

The structure of the twice-differential cross section for the incoherent neutron scattering (eq A1.7) remains invariant. Thus, in this step our task reduces to finding the function $f_1(k^2)$.

In general, the displacement $\mathbf{\Delta r}_m^{(d)}(\tau)$ of a molecule at time τ is the sum of two independent contributions:

$$\mathbf{\Delta r}_m^{(d)} = \mathbf{\Delta r}_m^{(c)} + \mathbf{\Delta r}_m^{(1)} \qquad \text{(A1.18)}$$

where the first term $\mathbf{\Delta r}_m^{(c)}$ describes the collective drift of a molecule in the field of thermal hydrodynamic fluctuations and the second term $\mathbf{\Delta r}_m^{(1)}$ the displacement of a molecule with respect to its nearest neighbors.[18] In other words, $\mathbf{\Delta r}_m^{(d)}$ is the sum of the collective and one-particle contributions. Because of this, we can write

$$f_1(k^2) = f_1^{(c)}(k^2)\cdot f_1^{(1)}(k^2)$$

where

$$f_1^{(c)}(k^2) = \left\langle \exp(\mathrm{i}\mathbf{k}\cdot\mathbf{\Delta r}_m^{(c)})\right\rangle \quad \text{and} \quad f_1^{(1)}(k^2) = \left\langle \exp(\mathrm{i}\mathbf{k}\cdot\mathbf{\Delta r}_m^{(1)})\right\rangle$$

As shown in refs 15 and 16, the collective transport is caused by the transverse modes in liquids and has diffusion character. Therefore, $f_1^{(c)}(k^2)$ takes the form appropriate for diffusion behavior:

$$f_m^{(c)}(k^2) = \exp(-6D_c k^2\tau) \qquad \text{(A1.19)}$$

where D_c is the collective part of the self-diffusion coefficient.[15,16]

In regard to the function $f_1^{(1)}(k^2)$, averaging it over the angular variables gives

$$f_1^{(1)}(k^2) = \left\langle \frac{\sin k\Delta r_m}{k\Delta r_m}\right\rangle$$

It seems to be natural to model the distribution $\mathbf{\Delta r}_m$ of a molecule during the typical time of an elementary diffusion act by the Gaussian distribution

$$W(\mathbf{\Delta r}_m) = \left(\frac{\gamma}{\pi}\right)^{3/2}\exp(-\gamma\Delta r_m{}^2) \qquad \text{(A1.20)}$$

in which $\gamma = (4l_0{}^2)^{-1}$, where to an order of magnitude, $l_0 \leq a$. Then

$$f_1^{(1)}(k^2) = \exp(-k^2 l_0^2)$$

Since our approach is correct only for $kl_0 \leq ka \ll 1$ (see eq A1.11), practically with the same accuracy we can write:

$$f_1^{(1)}(k^2) \approx \frac{1}{1 + k^2 l_0^2} \qquad \text{(A1.21)}$$

Precisely such an expression is obtained from the jump diffusion model.[19] However, the last imposes restrictions on the character of the thermal motion that are too hard. In particular, the typical time for a displacement by l_0 cannot be smaller than τ_s. Therefore, the interpretation of l_0 as the average length of a jump is not satisfactory, and averaging with the Gaussian distribution A1.20 seems to be preferable.

The quantity $(l_0^2)/\tau$ has the meaning of the one-particle contribution to the self-diffusion coefficient, since $D_s^{(1)} = \langle(\Delta r_m^{(d)})^2\rangle/6\tau \rightarrow l_0^2/\tau$. Thus,

$$k^2 l_0^2 \rightarrow \tau D_s^{(1)} k^2$$

and eq A1.17 for the half-width of the diffusion peak takes the form

$$\gamma_D(k^2) = \frac{1}{\tau}\left(1 - \frac{\exp(-D_c k^2 \tau)}{1 + \tau D_s^{(1)} k^2}\right) \qquad \text{(A1.22)}$$

This is similar to the expression

$$\gamma_D^{(SS)}(k^2) = \frac{1}{\tau}\left(1 - \frac{\exp(-2W)}{1 + \tau D_s k^2}\right) \qquad \text{(A1.23)}$$

obtained in ref 13 with the help of several too-detailed assumptions that cannot be justified from a physical point of view. In particular, they lead to an influence of the oscillation motion on the half-width of the diffusion peak (see eq A1.23) that is especially problematic. Our result, eq A1.22, is free from this shortcoming.

In accordance with eq A1.10, the region of applicability of our theory is restricted by the inequality $\tau D_s^{(1)} k^2 \ll 1$, or $l_0^2 k^2 \ll 1$, so it is appropriate to expand the half-width of the diffusion peak (eq A1.22) as a power series in $\tau D_s^{(1)} k^2$:

$$\gamma_D(k^2) \approx D_s k^2 - \tau_0 D_s^{(1)2} k^4 + \tau_0^2 D_s^{(1)3} k^6 + ... \qquad \text{(A1.24)}$$

where $D_s = D_s^{(1)} + D_c$ has the meaning of the full self-diffusion coefficient. It should be noted that eq A1.24 follows from eq A1.22 as a result of the condition $\tau_1 \ll \tau_0$ and the additional assumption about the smallness of D_c in comparison with D_s ($D_c \ll D_s$). This question is discussed in detail in ref 18. It is evident that the structure of eq A1.24 is in full agreement with eq A1.13.

According to eq A1.24, the half-width of the diffusion peak deviates from the linear dependence on k^2 [i.e., the expression $\gamma_D(k^2) = D_s k^2$] that is inherent in the simplest diffusion model. Such behavior of $\gamma_D(k^2)$ is in agreement with experimental results.[2−12]

By comparing eq A1.24 with experimental data for the half-width of the diffusion peak, we can determine all of the essential parameters of the thermal motion: D_s, $D_s^{(1)}$, and τ_0. This procedure is correct if the experimental data for $\gamma_D(k^2)$ are obtained over the range restricted by the inequality A1.11, $k \ll 1$ Å^{-1}. The use of experimental data acquired outside this range can lead to considerable errors in the values of the key model parameters.

The collective part of the self-diffusion coefficient for the molecules is determined as

$$D_c = D_s - D_s^{(1)} \qquad \text{(A1.25)}$$

It necessary to emphasize that all results presented in this appendix are applicable for $T \leq T_H$. At higher temperatures, the crystal-like model of the thermal motion in water becomes invalid. The molecular oscillations have no regular character, and the thermal motion in water approaches argon-like behavior.

Appendix 2.

Half-Width of the Neutron Scattering Peak Outside the Region of Applicability of the Diffusion Approximation.

The half-width of the diffusion peak is obviously limited by the upper bound $\bar{\gamma}_D \approx D_s k^2|_{k\approx 1/a} \approx 10^{11}$ s^{-1}. In fact, the permissible values of the half-width that can be determined with the help of the diffusion approximation belong to the more narrow frequency interval

$$\gamma_D \approx D_s k^2 \leq \gamma_* \approx 10^{10}\ \text{s}^{-1} \qquad \text{(A2.1)}$$

Outside this interval [i.e., for $k \gg (\gamma_*/D_s)^{1/2} \approx 0.3$ Å^{-1}], the half-width of the neutron peak should be determined on the basis of other representations.

Here we pay attention to the fact that during a time interval on the order of τ, water and water + electrolyte solutions are microinhomogeneous: spatial regions with crystal-like structure are formed in them. The size of such regions can be estimated as $r_s \approx c\tau \approx 10$ Å, where c is the longitudinal sound velocity. On the other hand, considering the transverse modes, we can write $r_t \approx c_t\tau_M \approx 10$ Å, where $c_t \approx (\nu/\tau_M)^{1/2}$ is the high-frequency transverse sound velocity, ν is the kinematic shear viscosity, and τ_M is the Maxwell relaxation time for the shear tension. In accordance with refs 15, 16, and 18, the typical size of the crystal-like region, $r_t \approx (\nu\tau_M)^{1/2}$, is proportional to the radius of the so-called Lagrange particle, $r_L = 2(\nu\tau_M)^{1/2}$.

It is noteworthy that the computer simulations of thermal motion in water in ref 39 and the analysis of those results in ref 40 have confirmed our conclusion about the microinhomogeneous structure of water in the supercooled region and near the melting point.

A Lagrange particle drifts randomly, like a Brownian particle, in the field of thermal hydrodynamic fluctuations. During the time $0 < t < \tau$, a molecule moves together with the corresponding Lagrange particle. The main contribution to the similar drift is caused by transverse modes.[15,16] It is very essential that the characteristic decay time $t_d \approx 1/\nu k^2$ of these modes for $k \gg (\nu\tau)^{-1/2} \approx 0.1$ Å^{-1} be significantly smaller than $\tau_M \approx \tau$. Therefore, the displacement of a molecule connected with the motion of the Lagrange particle can be represented in the form

$$[\mathbf{\Delta r}(t)]_t = \mathbf{u}_L t \qquad (t \ll \tau_M \approx \tau)$$

where $\mathbf{u}_L$ is the velocity of the Lagrange particle. Therefore, the mean square displacement of a molecule can be represented as

$$\left\langle [\Delta r(t)]_t^2 \right\rangle = \frac{2k_BT}{m_L} t^2 \qquad \text{(A2.2)}$$

where

$$m_L = \frac{4}{3}\pi r_L{}^3 \rho$$

is the mass of the Lagrange particle. To an order of magnitude, the maximal displacement of a molecule in a time $2\tau_M$ is equal to $(k_BT/\eta r_L)\tau_M \ll a^2$. Therefore

$$\langle \exp[i\mathbf{k}\cdot\mathbf{\Delta r}_t(t)] \rangle \approx \exp\left(-\frac{2k_BT}{m_L}k^2t^2\right)$$

for $k > k_L$, where $k_L = r_L^{-1} \approx (0.1$ to $0.3)$ Å^{-1}.

This character of the time dependence of the intermediate function corresponds to the following expression for the half-width of the neutron peak:

$$\gamma_n(k) \approx 2\sqrt{\frac{2k_BT}{m_L}}k \qquad (k > m_L \approx \sqrt{\gamma_*/D_s}) \qquad \text{(A2.3)}$$

At $k \approx 1$ Å^{-1}, the half-width γ_n takes the value $\gamma_n \approx 10^{11}$ s^{-1}, which agrees with experimental data.[2−12] The formula A2.3 allows us to obtain an independent estimate of the mass of the

Lagrange particle or its radius. In fact, this circumstance is especially important.

The contribution of the sound modes to the displacement of a Lagrange particle for short times $t \ll \tau_M \approx \tau$ is manifested analogously to eq A2.2. Therefore, for $k > (\gamma_*/D_s)^{1/2}$, eq A2.3 becomes

$$\gamma_n(k) \approx 2\sqrt{\frac{3k_BT}{m_L}}k \qquad (k > \sqrt{\gamma_*/D_s}) \qquad \text{(A2.4)}$$

Typically, sound modes are correctly determined up to wave vectors $\mathbf{k}$ for which $k < k_*$, where

$$k_* = \frac{mc}{\hbar} \qquad \text{(A2.5)}$$

in which m is the molecular mass and c is the sound velocity. Such an estimate follows from the structure of spectra for the longitudinal excitations of liquids,[41,42] including collective and one-particle contributions. To an order of magnitude for liquid water,

$$k_*(H_2O) \approx 10\ \text{Å}^{-1} \qquad \text{(A2.6)}$$

Thus, the applicability region of eq A2.4 is restricted by the inequality

$$\sqrt{\frac{\gamma_*}{D_s}} < k < k_* \qquad \text{(A2.7)}$$

For $k > k_*$, the character of the wave-vector dependence of the half-width radically changes:

$$\gamma_n(k) \approx 2\sqrt{\frac{3k_BT}{m}}k \qquad (k > k_*) \qquad \text{(A2.8)}$$

The crossover of the half-width from the diffusion expression (eq A1.24) to eq A2.4 is really observed at $k_{cr} \approx (\gamma_*/D_s)^{1/2}$, as was first noted in ref 5.

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